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Moffett Field, CA 94035-1000

# Analysis of Trace Halocarbon Contaminants in Ultra High Purity Helium

LARRY L. FEWELL

*Ames Research Center*

## Summary

This study describes the analysis of ultra high purity helium. Purification studies were conducted and contaminant removal was effected by the utilization of solid adsorbent purge-trap systems at cryogenic temperatures. Volatile organic compounds in ultra high purity helium were adsorbed on a solid adsorbent-cryogenic trap, and thermally desorbed trace halocarbon and other contaminants were analyzed by combined gas chromatography-mass spectrometry.

## Introduction

Trace analyses of permanent gases by gas chromatography involving detectability at the parts per million (ppm) to parts per billion (ppb) concentration level using helium ionization detectors (HID) place special requirements on carrier gas purity. The HID is a universal or nonselective detector and responds to permanent gases as well as hydrocarbons and complex organic compounds. Although the HID is a highly sensitive, nonselective detector, its use has been limited due to requirements for a contaminant free chromatographic system (refs. 1 and 2). The ionization process is based on the conveyance of metastable helium's excitation energy (19.8 eV) to eluting molecules. This is based on the principle (Penning Ionization, ref. 1) that the metastable helium atom will ionize all compounds with a lower ionization potential than that of the metastable helium atom's excitation energy. The primary electrons emitted by the  $\text{Ni}^{63}$  source impacts or collides with helium molecules, creating metastable helium atoms. The metastable helium atoms then de-excite or impart their excitation energy via collisions with eluting compounds. In this process all compounds having ionization potential lower than that of the metastable state of helium will be ionized. The net result of these processes is an increase in the ionization current. One would therefore draw the conclusion that the ionization mechanism is directly dependent on the number or population of metastable atoms produced and their lifetimes. These mechanisms are a consequence of the primary electron energy (eV) and the intensity of the applied electric field. These mechanisms, which produce

ultra sensitivity to all compounds, also place stringent requirements on the purity of the helium carrier gas for optimum performance of the HID. Impurities in the helium or from the system will impact detector operating parameters such as background current, noise, magnitude of response, signal polarity, and the overall stability of the detector. The purer the helium carrier gas, the higher the applied voltage without resulting in an increase in the background current and noise level, which in turn allows for the application of more applied voltage and greater sensitivity. The concentration and type of impurity in the helium carrier gas cause changes in the background current. Impurities affect peak shape and polarity. Andrawes and Gibson (ref. 2) demonstrated that as the concentration of added impurities increases, the negative peaks decreased and some became positive. Some contaminant species impact other contaminants, causing anomalous detector responses. For example, increasing amounts of nitrogen added to the helium carrier gas containing 4.5 ppm neon caused the negative response to neon to become positive. Ideally a positive detector response should be indicated for all gases, except neon, when pure helium is the carrier gas. The ionization potential of neon (21.5 eV) is higher than the metastable energy of helium (19.8 eV) and consequently cannot be ionized by metastable helium atoms ( $\text{He}^*$ ). Any impurity, whether ionizable or non-ionizable, will increase or decrease the background current, respectively. In the strictest sense of the term, a 100% pure gas can be defined as the partial pressure of the carrier gas equaling the total pressure of the system. In practical terms this is quite difficult and the expense of production would be considerable. In our laboratories we use helium carrier gas assayed by the manufacturer (private communication, Scott Specialty Gases, Fremont, Calif.) to be 99.9999% pure. Contaminants may not only be in the carrier gas cylinder but can be introduced into the carrier gas stream from the components of the chromatograph such as tubing, column packing, and fittings.

In this study the utilization of a solid adsorbent purge-trap technique for the removal and isolation of halocarbon impurities in UHP helium and their identification by

thermal desorption gas chromatography-mass spectrometry are described.

The author gratefully acknowledges the technical assistance of Melvin Walker, Jr., Morehouse College, Atlanta, Georgia; and Peter T. Palmer, TGS Technology, Inc., Mountain View, California.

## Experimental

The gas chromatograph consists of three Carle Instrument ovens in parallel. The oven housing a Haysep "A" packed column (12 ft  $\times$  1/16 in. stainless steel) for the separation of permanent gases and a Haysep "N" packed column (12 ft  $\times$  1/16 in.) for the separation of hydrocarbons is kept at a temperature of 25°C. The second oven contains a Haysep "P" packed column (5 ft  $\times$  1/16 in.) and is kept at a temperature of 101°C for the separation of polar compounds. All volatiles are introduced into each column by a six port Carle gas sampling valve via a three way splitter. One-third of the volatiles are chromatographed on each column. The third oven houses the three HIDs and is kept at 105°C. Detector construction and associated electronics were described in an earlier report (ref. 3). A molecular sieve 5A column (4 ft  $\times$  1/4 in. stainless steel) was conditioned at 300°C at a nitrogen flow rate of 60 cc/min. for 48 hr. The molecular sieve column was immersed in a Dewar of isopropanol kept at -82°C (controlled by a Neslab CC-100 immersion cooler) and placed in the ultra high purity (UHP) helium carrier gas line. Each port of the molecular sieve trap was plugged with Swagelok<sup>TM</sup> fittings prior to removal from the

Dewar. The molecular sieve was removed from the column and placed in a glass tube and placed in the thermal desorption instrument (Tekmar 6000 Automatic On-Line Desorber, Tekmar, P.O. Box 42956, Cincinnati, OH 45242-9571) where the solid adsorbent (molecular sieve adsorbates) were measured by purge-and-trap analysis (PTA). The gas chromatography-mass spectrometry-data system (GC-MS-DS) utilized in this study was a Finnigan MAT ITS40 GC-MS-DS system. The volatile organic compounds (VOCs) were cryo-focused onto a fused silica capillary 25 m  $\times$  25 mm ID, 5% phenyl, 95% methyl silicone column and analyzed via GC-MS. After sparging by UHP helium, the purged VOCs were collected from the UHP helium purge gas onto the adsorbent silica trap. When the purging process was completed, the trap was simultaneously heated and backflushed with helium carrier gas. The backflushing procedure effectively sweeps the VOCs from the heated trap into the combined gas chromatograph-mass spectrometer (GC-MS) for separation and identification. This provided a qualitative determination of the cumulative trace contaminants removed from five UHP helium cylinders.

## Results and Discussion

The maximum allowable level for 99.9999% (referred to as 6-9s) purity helium impurities is 1.0 ppm. Variances in the amount of impurities per cylinder filling are indicated in table 1 (private communication, Scott Specialty Gases, Fremont, Calif.). The total impurities per cylinder were less than 1.0 ppm.

Table 1 Variances in amount of impurities per cylinder filling

Impurities, ppm	Cylinder ID number				
	11,326	6,204	16,577	12,033	13,244
Argon	0.05	0.05	0.05	0.05	0.05
Carbon dioxide	0.05	0.05	0.05	0.05	0.05
Carbon monoxide	0.05	0.05	0.05	0.05	0.05
Halocarbon	0.01	0.01	0.01	0.01	0.01
Hydrogen	0.05	0.05	0.05	0.05	0.05
Methane	0.05	0.05	0.05	0.05	0.05
Neon	0.05	0.05	0.41	0.05	0.05
Nitrogen	0.21	0.07	0.09	0.11	0.06
Oxygen	0.05	0.05	0.05	0.05	0.05
Water	0.02	0.05	0.06	0.05	0.05
Total	0.59	0.48	0.87	0.52	0.47

The system utilized by the vendor in the final purification step for obtaining 6-9s helium prior to cylinder filling is to pass the helium through a mole sieve liquid nitrogen trap for the removal of remaining trace contaminants including neon (fig. 1). The concentration of the neon contaminant (0.41 ppm) in cylinder no. 1A-016577 is quite high for some as yet inexplicable reason. The variability of total contaminants was certified from batch to batch to be no greater than 100 ppb with a relative standard deviation (RSD) between batch quantities of 98 ppb and 43 ppb between cylinders comprising a batch (private communication, Scott Specialty Gases, Fremont, Calif.). The cryocool immersion-trap system (fig. 2) in our helium carrier gas line served for the further purification of 6-9s helium. After a year of continuous operation in which the contents of five UHP helium cylinders were expended, the trap was replaced and the molecular sieve removed. An aliquot was taken for PTA combined GC-MS analysis.

The VOCs detected consisted of eight halocarbon and two aromatic compounds (table 2). The total ion chromato-

graph (TIC, fig. 3) shows the eluting water background after which the ion current drops substantially prior to the elution of the first VOC. The first eluting VOC is the major constituent (63%) of the mixture and was identified as 2-chloro-1-(difluoromethoxy)-1,1,2 trifluoroethane based on its mass spectrum (fig. 4, top graph) and computer library search. The mass spectra (fig. 4, middle graph) of the second major VOC (peak 3, fig. 3) indicates a chlorine containing hydrocarbon showing typical isotopic clustering at  $m/z$  101, 103, and 105 and is identified as trichlorotrifluoroethane. The third major VOC eluted (peak 2, fig. 3) was identified as 3-chloro perfluoro-propene or 3-chloro-1,1,2,3,3-pentafluoro-1-propene (fig. 4, bottom graph). Minor analytes are described by attenuated TIC (fig. 5). Mass spectra (fig. 6) were also verified by the data system library search of these minor VOC constituents.

These analyses of high purity research grade helium (99.9999%) were for the purpose of identifying trace contaminants in ultra high purity carrier gas for our flight instruments.

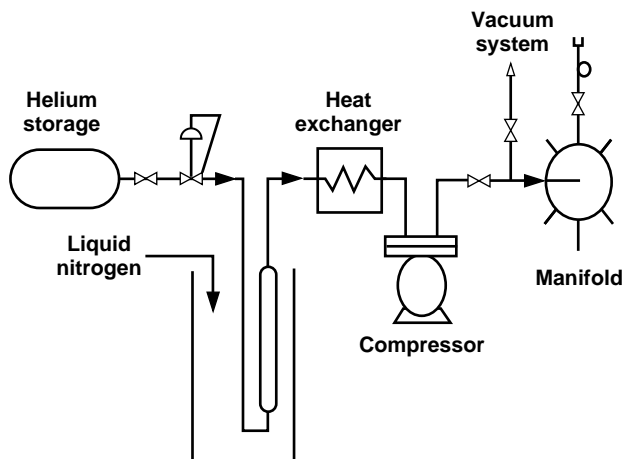


Figure 1. Batch helium purification system. (Courtesy of Scott Specialty Gases.)

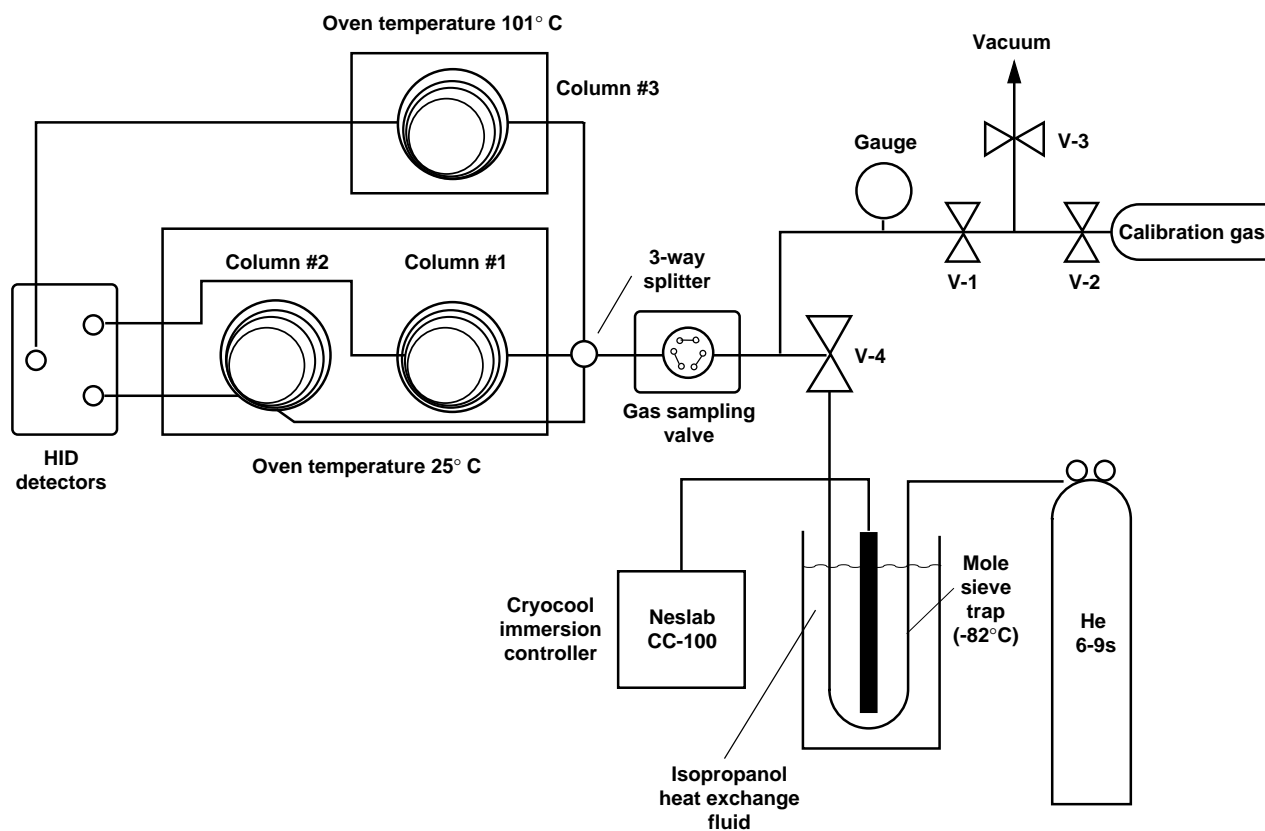


Figure 2. Cryocool immersion pre-column trap for the removal of trace contaminants from UHP helium carrier gas.

Table 2. VOCs detected

Peak No.	Retention time, sec	Compound	Structure	F.W.	Concentration, ppt <sup>a</sup>	Percent of total VOCs
1	722	2-chloro-1-(difluoro methoxy)-1,1,2-trifluoroethane	$\text{CHF}_2\text{-O-CF}_2\text{-CHClF}$	184	154.0	63.00
21	78	1,1,2-trichloro-1,2,2-trifluoroethane	$\text{CCl}_2\text{F-CClF}_2$	186	21.5	8.70
3	89	3-chloro-1,1,2,3,3-pentafluoro-1-propene	$\text{CF}_2\text{-CF-CClF}_2$	166	43.1	17.60
4	100	dichlorodifluoromethane	$\text{CCl}_2\text{F}_2$	120	7.5	3.10
5	125	trichloroethane	$\text{CCl}_3\text{-CH}_3$	132	2.7	1.10
6	133	benzene	$\text{C}_6\text{H}_6$	78	1.8	0.73
7	161	1,1,2-trichloroethane	$\text{CCl}_2\text{=CHCl}$	130	1.9	0.78
8	230	1-chloro-1,1,2,2-tetrafluoroethane	$\text{CClF}_2\text{-CHF}_2$	136	4.5	1.80
9	239	toluene	$\text{C}_7\text{H}_8$	92	3.1	1.30
10	310	tetrachloroethylene	$\text{CCl}_2\text{=CCl}_2$	164	4.7	1.90

ppt = parts per trillion.

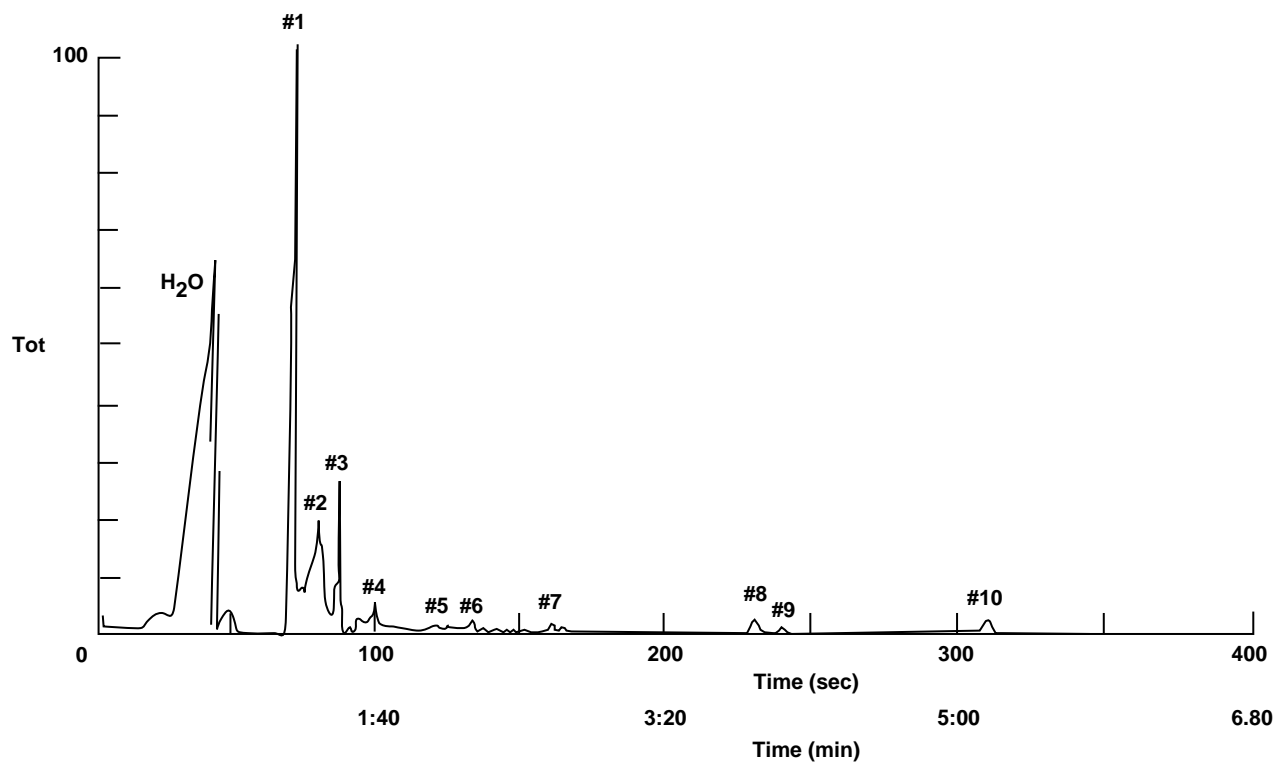
<sup>a</sup>Based on RIC/calibration.

Figure 3. Total ion current chromatogram plot of pre-column trapped VOCs.

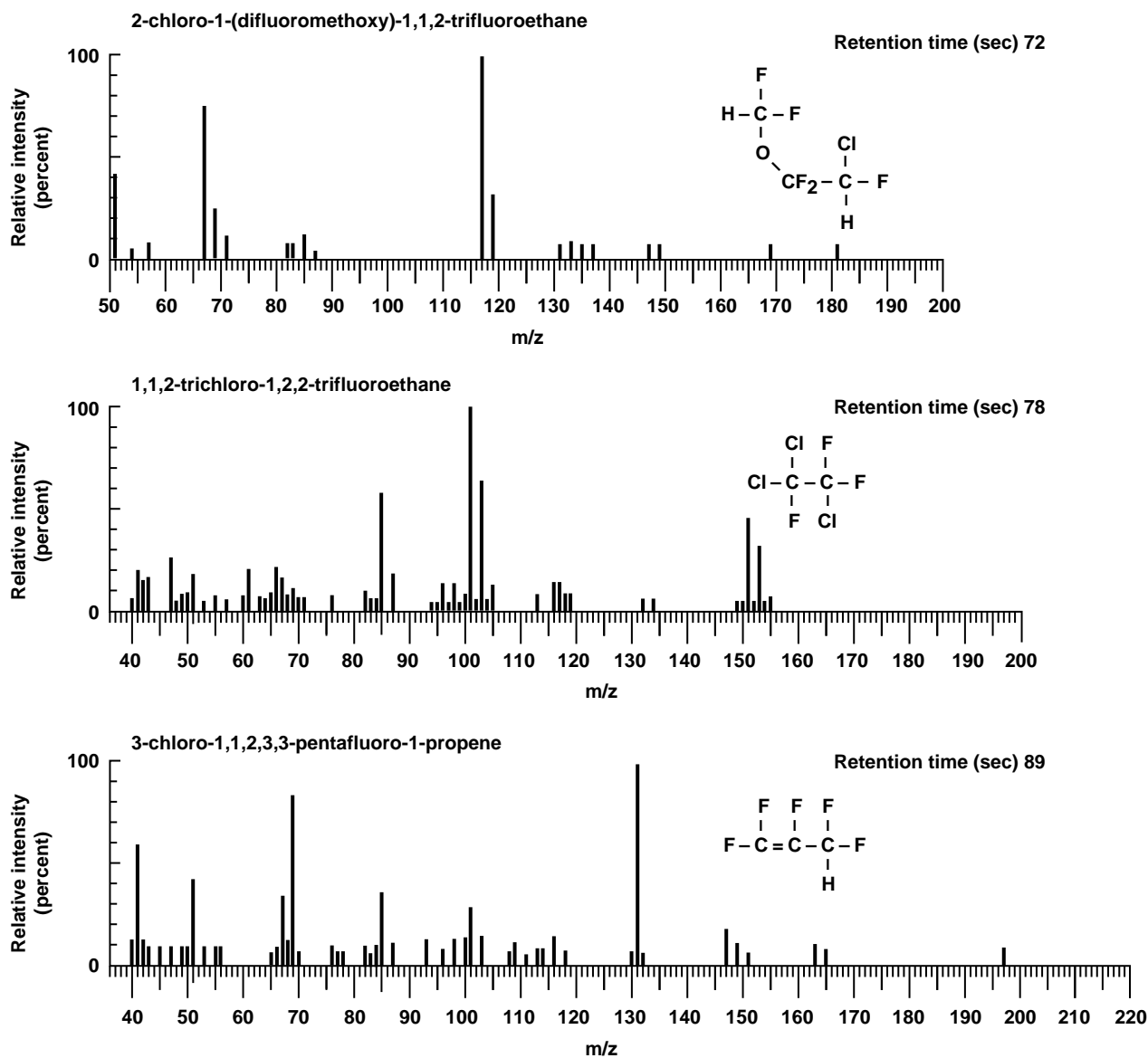


Figure 4. Mass spectra of major halocarbon compounds in trapped VOCs.



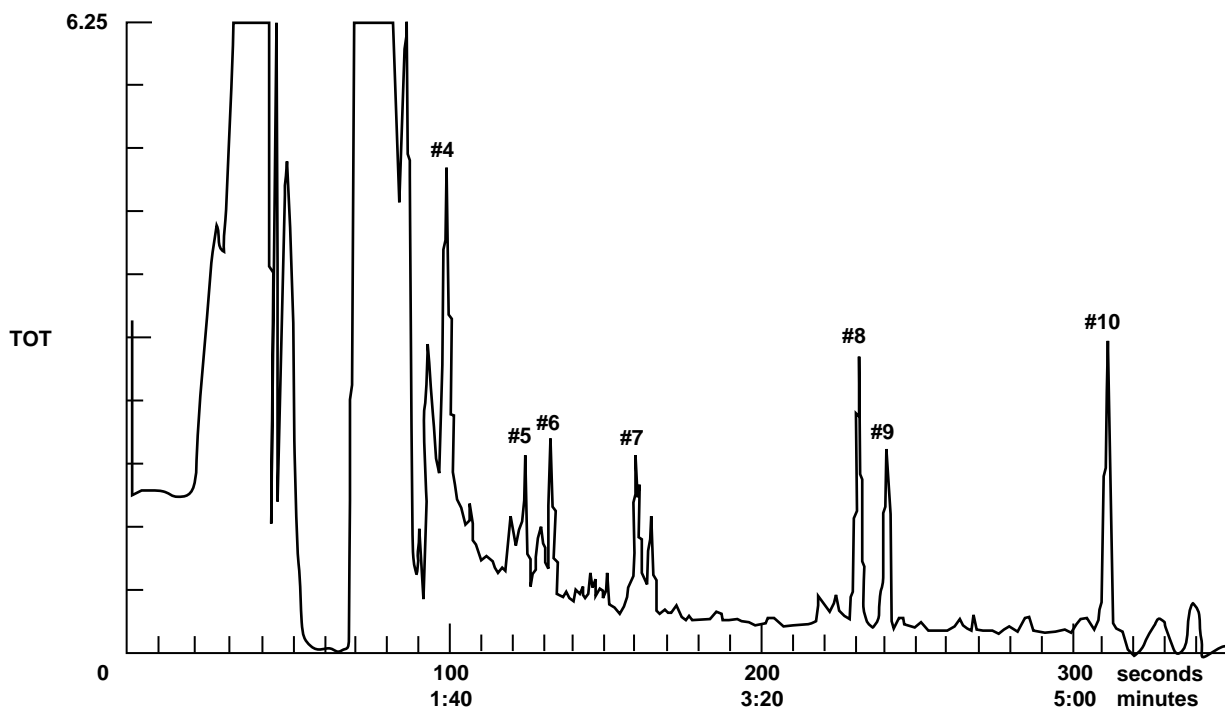


Figure 5. Attenuated total ion current plot of trapped VOCs.

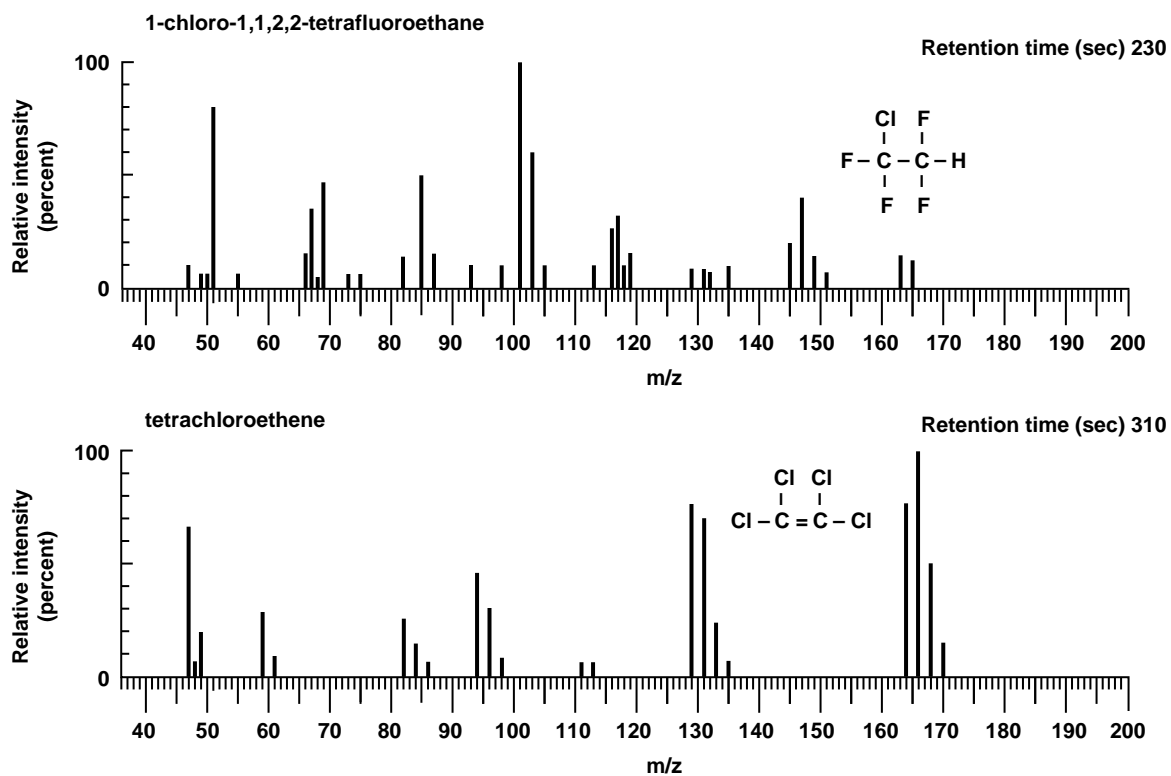


Figure 6. Mass spectra of minor halocarbon compounds in trapped VOCs.

## Conclusions

The detection of halocarbon contaminants in UHP helium was unexpected, puzzling, and interesting. Communications with the gas supplier indicated that in order to minimize leak rates during cylinder filling and to ensure sealing integrity between the cylinder valve and the manifold, Kel-F tips were utilized to ensure minimum leakage. Kel-F is an engineering thermoplastic, a homopolymer of chlorotrifluoroethylene ( $-\text{CFCl}-\text{CF}_2-$ )<sub>n</sub> or polychlorotrifluoroethylene (PCTFE) which has a variety of applications such as valve seats, molded seals, and stems and gaskets because of its mechanical (high compressive strength) and low temperature properties. The polymer is resistant to most chemicals and oxidizing agents, exhibiting very slight swelling in halogenated compounds, esters, ethers, and aromatic solvents. The presence of trace quantities of halocarbon compounds in UHP helium is attributed to the use of Kel-F tips and are most likely due to impurities from the polymerization of chlorotrifluoroethylene due to the incomplete removal of

minute quantities of free radical initiator residues from the latex suspension or related trace impurities that can result in chain degradation processes.

The gas supplier periodically analyzes cylinders by gas chromatography using an electron capture detector. Average values for halocarbon impurities per cylinder of UHP helium were 200 parts per trillion (ppt). However their analyses did not involve the separation and individual identification of each halocarbon constituent.

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